

AD-D016 224



Serial No. 126,869

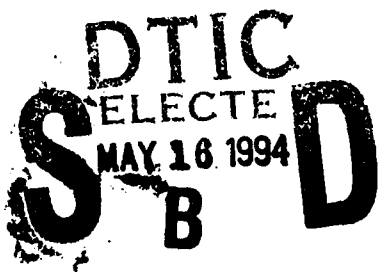
Filing Date 27 September 1993

Inventor Fred Pearlstein  
Vinod S. Agarwala

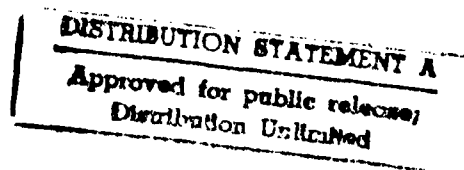
NOTICE

The above identified patent application is available for licensing.  
Requests for information should be addressed to:

OFFICE OF NAVAL RESEARCH  
DEPARTMENT OF THE NAVY  
CODE OCCC3  
ARLINGTON VA 22217-5660



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



94-14535



SPX

94 5 13 118

1           TRIVALENT CHROMIUM CONVERSION COATINGS FOR ALUMINUM

5           STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

10           BACKGROUND OF THE INVENTION

This invention relates to a method of treating metal surfaces to enhance corrosion resistant and paint bonding characteristics and more particularly, relates to trivalent chromium coatings for aluminum and aluminum alloys and, sealers  
15 for anodized aluminum substrates.

It is generally known to treat the surfaces of metals, such as zinc, cadmium, or aluminum with aqueous chromate (hexavalent chromium) solutions which contain chemicals that dissolve the surface of the metal and form insoluble films  
20 known as "chromate conversion coatings." These chromium coatings, are corrosion resistant and protect the metal from various elements which cause corrosion. In addition, it is known that chromate conversion coatings generally have good

1 paint bonding characteristics and, therefore, provide an  
excellent base for paint or other finishes.

Although the aforementioned coatings enhance corrosion  
resistant and paint bonding properties, the coatings have a  
5 serious drawback, i.e., the toxic nature of the hexavalent  
chromium constituent. This is a serious problem from two  
viewpoints, one being the handling of the solution by operators  
and the other, the disposal of the used solution. The disposal  
problem, however, can be mitigated by reducing the hexavalent  
10 chromium to the comparatively innocuous trivalent form before  
disposal. This method is expensive and therefore can be a  
major cost factor in the overall metal treating process.  
Therefore, it is highly desirable to have coatings which are  
substantially free of hexavalent chromium, but at the same time  
15 capable of imparting corrosion resistant and paint bonding  
properties which are comparable to those imparted by  
conventional chromium coatings.

Of particular interest is the use of chromate conversion  
coatings on aircraft aluminum alloys due to the excellent  
20 corrosion resistance and the ability to serve as an effective  
base for paint. The baths used to develop these coatings  
contain chromates, i.e., hexavalent chromium, and it is the  
residual chromates in the coating that is largely responsible  
25 for the high degree of corrosion inhibition. However, these  
same chromates are highly toxic and their presence in waste

1 water effluents is severely restricted. It would therefore, be  
desirable to provide a coating for aluminum and its alloys and  
for sealing of anodized aluminum utilizing relatively non-toxic  
chemicals that could serve as an alternative to the toxic  
5 hexavalent chromate coatings.

In the prior art, trivalent chromium baths (U.S. Patent  
No. 4,171,231) have been used to produce coatings on zinc and  
zinc plate to provide a decorative "clear to light blue finish"  
which are characterized as having superior corrosion  
10 resistance. These baths contain "trivalent" chromium as  
substantially the only chromium ion, with a fluoride ion, an  
acid other than nitric acid and an oxidizing agent. The  
operating range of the baths is at a pH between about 2 to 4  
and preferably between 1 to 3. The baths are used to achieve a  
15 single-dip chromate finish on all types of zinc plate. The  
implication is that the presence of the oxidizer, in situ,  
produces hexavalent chromium on the zinc surface without any  
oxidation or conversion of the trivalent chromium in the bath  
to the hexavalent form. Patentee discloses that without the  
20 oxidizing agent in the bath, corrosion resistance was poor,  
i.e., extensive corrosion after 24 hours with a 5% salt spray  
exposure, whereas with the oxidizing agent in the bath there  
was 0-10% of white corrosion and some panels were free of white  
salt after 50 hours of salt spray exposure.

25

1        This invention, in comparison, utilizes trivalent chromium  
as the only chromium ion in the bath with a fluoride ion,  
preferably from a complex compound such as a fluosilicate at a  
specific pH range. It was found that the addition of an  
5       oxidizing agent such as peroxide to the bath, in situ, slowly  
oxidized the trivalent chromium to the toxic hexavalent form.  
This conversion to the hexavalent form is contrary to the  
method used by this invention; namely, utilization of a bath  
composition completely free of hexavalent chromium.

10                    SUMMARY OF THE INVENTION

         This invention relates to a process for preparing a  
corrosion-resistant trivalent chromium coating on aluminum,  
aluminum alloy and for sealing of anodized aluminum substrates  
which comprises treating said substrates with an acidic aqueous  
15       solution containing from about 0.2 to 3.0 g/l of trivalent  
chromium as a water soluble compound, about 0.05 to 1.5 g/l  
fluoride as a water soluble fluoride compound and a sufficient  
amount of an alkaline reagent to maintain the aqueous solution  
at a pH ranging from about 4.0 to 5.5 sufficient to convert the  
20       trivalent chromium compounds to more basic soluble trivalent  
compounds thereby forming a trivalent-chromium coating on said  
substrates. However, alkali should not be added beyond the  
point where a persistent cloudiness (precipitation) forms in  
the bath. Fluoride is not required when used solely for  
25       sealing anodized aluminum. The trivalent-chromium coatings

1 formed on the aluminum substrates including sealing the  
anodized aluminum in accordance with this invention may be  
further improved by subsequently post-treating the trivalent  
chromium coating with effective amounts of an oxidizing agent,  
5 e.g., solution of peroxide, whereby only less than about 2.0  
percent by weight of the trivalent coating is converted to the  
hexavalent form on the aluminum substrate.

It is therefore an object of this invention to provide a  
novel chromium-containing solution for treating aluminum,  
10 including anodized aluminum which contains no hexavalent  
chromium.

It is another object of this invention to provide a  
composition for treating aluminum which contains only trivalent  
chromium.

15 It is still another object of this invention to provide a  
trivalent chromium-containing solution wherein said chromium  
has little or no tendency to precipitate from the solution.

It is a further object of this invention to provide a  
method of preparing trivalent chromium chemical-conversion  
20 coatings on aluminum and a seal on anodized aluminum surfaces.

It is a further object of this invention to provide a  
method of sealing anodized aluminum to obtain improved  
corrosion resistance.

1           These and other objects will become apparent to those skilled in the art from the description of the invention as follows.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

5           In producing a corrosion-resistant coating on an aluminum surface, the surface is first cleaned of soils and oxides which can interfere with the coating process. The surface can be cleaned by any convenient method known to the art. A suitable cleaning process uses an alkaline cleaner. Subsequent to the  
10 cleaning, a water rinse is employed and a deoxidizer may be used to remove any oxides that may be present on the metal surfaces. Continuous overflowing water rinses, for example, are suitable to remove any residual materials from the surface. It is only necessary that the surface be clean of all organic  
15 and inorganic residue. Subsequent to the cleaning and rinsing, the aluminum surface is treated with the trivalent chromium coating solution of this invention.

          Various methods of contacting the aluminum surface with the coating solution commonly employed in the metal coating art  
20 is acceptable. For example, the aluminum surfaces or substrates can be treated or contacted by spraying, dipping, roller coating, or the like. The chromium coating or sealer can be formed on the aluminum surface at temperatures ranging from about 16°C and about 90°C. Although the coating solution

1 or bath can be employed at temperatures in excess of 50°C, it  
is preferred that the coating operation be performed at or  
slightly above room temperature, i.e., between about 20°C and  
42°C.

5 More specifically, the process of this invention requires  
a certain amount of alkali (usually sodium hydroxide) to be  
added to the bath to promote hydrolysis and conversion of the  
trivalent chromium compounds to more basic forms. The proper  
amount of alkali (usually as 0.5N to 6N NaOH solution) to be  
10 added to a bath is determined by dispensing the alkali to the  
bath with agitation, while maintaining a pH between 4 and 5.5  
for about 5 to 30 minutes or until a precipitate persists in  
the bath. The preferred pH range is between 4.1 to 4.7 for  
about 5 to 10 minutes. The coating of this invention when  
15 applied to aluminum will usually require 96 to 168 hours  
exposure to salt spray before the first appearance of white  
salts corrosion. This is without any hexavalent chromium in  
the bath. The absence of  $\text{Cr}^{+6}$  was determined by analysis of  
the bath by atomic absorption spectroscopy and the Hach Test  
20 Kit.

The process of this invention may include a post-treatment  
in a dilute oxidizer e.g., 10 ml/liter  $\text{H}_2\text{O}_2$  (30%) to further  
improve the corrosion resistance of the trivalent chromium-  
containing coating to about 168 to 336 hours of salt spray  
25 exposure. The primary treatment bath of this invention is free



1 of hexavalent chromium and since the post-treatment requires no  
rinse, there is no  $\text{Cr}^{+6}$  in the waste stream. Occasionally, it  
may be necessary to discard the post-treatment bath, but the  
quantity of  $\text{Cr}^{+6}$  contained in the bath is minuscule and will  
5 have virtually no environmental impact. Based on chemical  
analysis of a used post-treatment (peroxide) bath, the total  
hexavalent Cr content was found to be  $<0.01$  p.p.m. This value  
is below the allowable limits for occasional discharge and  
therefore presents no difficulties. The coatings applied to  
10 aluminum in accordance with this invention are under  $20 \text{ mg/ft}^2$   
and when a peroxide post-treatment is used, the amount of  $\text{Cr}^{+3}$   
and  $\text{Cr}^{+6}$  in the film are approximately  $3.5 \text{ mg/ft}^2$  and  $0.05$   
 $\text{mg/ft}^2$ , respectively.

Further, in accordance with this invention corrosion  
15 resistant films or sealers can be applied to bare or anodized  
aluminum alloys (2024-T3 and 7075-T6) by immersion in baths  
consisting essentially of chromic sulfate and fluosilicate.  
About 10 minute immersion time at  $25^\circ\text{C}$  in the trivalent  
chromium bath was required to pass about 168 hours of salt  
20 spray corrosion resistance. However, immersion time can be  
reduced to as little as 2.5 minutes by mildly heating the bath  
i.e., temperature of about  $42^\circ\text{C}$ .

For comparison purposes, preliminary studies were  
conducted with molybdate solutions which produced thin colored  
25 films (presumably molybdic oxides) on immersed 7075-T6 Al-

1 alloy. These coatings had only slight salt spray resistance.  
With additives, corrosion resistance of about 24 hours salt  
spray exposure was achieved. For example, improvement was  
obtained with 5 minute immersion at 25°C in the following bath:

5 Example I

6 g/l  $\text{Na}_2\text{MoO}_4$   
4 g/l  $\text{Na}_2\text{SiF}_6$   
5 g/l  $\text{Na}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$   
2 g/l Benzotriazole

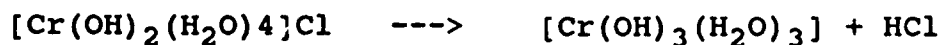
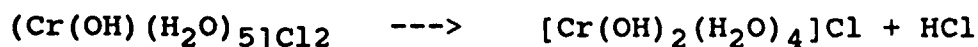
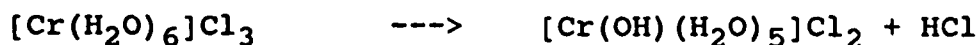
10 In another study, 20 minute immersion of 7075-T6 Al alloy  
in 20 g/l  $\text{Na}_2\text{CO}_3$  + 10 g/l  $\text{Na}_2\text{SO}_4$  solution at 50°C produced  
films of approximately 200 mg/ft<sup>2</sup> but with only a modicum of  
corrosion resistance. However, "sealing" these films in  
certain aqueous solutions improved the corrosion resistance.

15 For example, up to 72 hours salt spray resistance was attained  
by immersion of the rinsed carbonate film for 5 minutes in 10  
g/l  $\text{KMnO}_4$  solution at 50°C.

The study was then directed towards the use of trivalent  
chromium films. It was found that insoluble trivalent chromium  
20 compounds could indeed be formed on aluminum. It was also  
found possible to subsequently oxidize or post-treat the film  
whereby less than about 2.0% by weight of the trivalent  
chromium was converted to the hexavalent chromium. The post-  
treatment comprises a dilute solution of peroxide, e.g., 0.2 to  
25 about 40% by volume of  $\text{H}_2\text{O}_2$  (30%). Thus, it was found possible

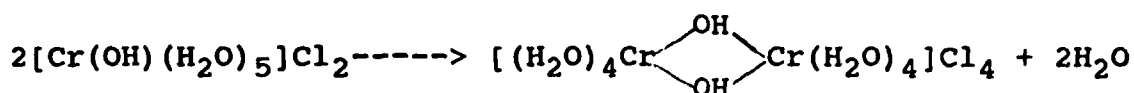
1 to attain corrosion resistant films or coatings comparable to  
other chromate coatings without the use of toxic hexavalent  
chromium. It is known that trivalent chromium is substantially  
less toxic than the hexavalent form.

5 More specifically, it was found that coating baths  
containing  $\text{Cr}_2(\text{SO}_4)_3$  and  $\text{Na}_2\text{SiF}_6$  when brought with  $\text{NaOH}$  to a  
pH, e.g., pH 4.0 to 5.5 near or slightly beyond precipitation  
of the basic compounds, were capable of forming light but  
visible films on Al-alloys which had significant corrosion  
10 resistance. When the pH was raised by addition of  $\text{NaOH}$ , the pH  
falls with time to considerably lower values. The reason being  
that trivalent chromium salts form coordination compounds of  
coordination number six. The hydrolysis of coordination  
complexes is accelerated by addition of alkali and forms  
15 successively in the following manner:



20 Analogous compounds are formed with the sulfate. The  
liberation of free acid accounts for the observed decrease in  
pH with time after alkali has been added to the chromium  
sulfate,  $\text{Cr}_2(\text{SO}_4)_3$ , solution. The molecular weights of the

1 compound may be increased by "olation" which is favored by heat and basicity as shown below:



5 Olation tends to promote hydrolysis by shifting the hydrolysis equilibrium. For example, a 12 liter bath was prepared with deionized water to which was added 4 g/l  $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$  [Fluka Co.; 26%  $\text{Cr}_2\text{O}_3$  and 23-24%  $\text{Na}_2\text{SO}_4$ ] and 0.4 g/l  $\text{Na}_2\text{SiF}_6$  with continuous stirring for about one hour to dissolve the chemicals. Then 20 ml/l of 0.5 N NaOH was added  
10 slowly with stirring. The bath was permitted to stand one week before use. Bath pH was over 5 when first prepared but after one week, the pH had decreased to about 3.7 and the bath was somewhat cloudy indicating precipitation of chromic hydroxide (hydrous chromic oxide). The bath was analyzed by atomic  
15 absorption analysis and found to contain 597 p.p.m. Cr which is about 84% of theoretical.

Aluminum alloys (7075-T6 and 2024-T3) panels, 3" x 5" x 0.030", were held on titanium racks and treated as follows:

- 20 a) Immersed 30 minutes in proprietary alkaline cleaner [53 g/l Turco 4215-NC-LT] at 55°C with air agitation and followed by room temperature running water rinses;

1           b) Immersed 15 minutes in proprietary nonchromate  
              deoxidizer [180 g/l Turco Smut-Go] at 25°C and  
              followed by room temperature running water rinses;

5           c) Immersed in 12 liter trivalent chromium bath as  
              described above at 25°C without agitation for 5, 10,  
              20 or 40 minutes and given one of the following post  
              treatments:

              (1) None

10           (2) 30 seconds in 10 ml/l  $H_2O_2$  (30%) in deionized  
              water at 25°C; drain dried without rinsing.

              (3) 30 seconds in 5 g/l  $KMnO_4$  at 25°C; water rinsed  
              and drain dried.

15           A scribe mark was made on each panel to ascertain whether  
              there was any tendency for self-healing as is achieved with  
              chromate conversion coatings. The panels were exposed to 5%  
              neutral salt spray, in accordance with ASTM B-117 Standard  
              Method. Visible films were produced on aluminum panels  
              immersed 10 or more minutes in the trivalent chromium bath;  
              pale tan at 10 minutes, pale violet at 20 minutes and pale blue  
20           at 40 minutes. The panels post-treated in permanganate were  
              somewhat darker colored.

              Film formation may initiate with attack (oxidation) of the  
              aluminum surface by fluoride-containing ions. The pH of the

1     interfacial solution is increased leading to intimate  
precipitation of insoluble hydrous chromic oxides on the  
surface. However, electrochemical studies indicate that the  
mechanism is more complex. The film weight of panels, immersed  
5     10 minutes in the trivalent chromium bath, was determined by  
stripping the film for 30 minutes in solution containing 35ml/l  
 $\text{H}_3\text{PO}_4$  (85%) + 20 g/l  $\text{CrO}_3$  at the boiling point, rinsing, drying  
and reweighing. The loss of weight averaged 3.8 mg per panel  
or 18 mg/ft<sup>2</sup>.

10           The results of salt spray exposures of panels treated  
various times in trivalent chromium bath are shown in Table I.  
After 336 hours exposure, the 7075-T6 panels that had been  
immersed 10, 20 or 40 minutes in trivalent chromium bath and  
provided with a permanganate post-treatment were free of  
15     corrosion or had only faint traces of corrosion. All 7075-T6  
panels provided with the peroxide post-treatment were only  
slightly corroded. Panels immersed in trivalent chromium bath  
for 5 or 10 minutes without any post-treatment had only slight  
corrosion while those immersed 20 or 40 minutes were somewhat  
20     more corroded. In general, best corrosion resistance was  
obtained when panels were immersed 10 minutes. There was  
little evidence of self-healing at the scribe mark made in the  
7075-T6 panels.

1

Table I

## Corrosion Ratings\* of Panels Treated in Trivalent

Chromium Bath After 336 Hours Salt Spray Exposure.

5

Immersion -----Post-Treatment -----  
 Time, 30 s, 10 ml/l 30 s, 5 g/l  $\text{KMnO}_4$   
 Minute None  $\text{H}_2\text{O}_2$  (30%) Water Rinsed

-----Al 7075-T6 Alloy-----

10

5	3	3+	3+
10	3	3+	5
20	2+	3	4+
40	2+	3	4+

-----Al 2024-T3 Alloy-----

15

5	0+	3	2
10	1	3	5
20	1+	2+	5
40	1	2+	5

## \* Rating Key

5 - No Corrosion

4 - Traces of Corrosion (incipient)

20

3 - Slight Corrosion (&lt;1% area affected)

2 - Moderate Corrosion (1 - 5% area affected)

1 - Considerable Corrosion (5 - 25% area affected)

0 - Extensive Corrosion (&gt;25% area affected)

25

The 2024-T3 panels after 336 hours salt spray exposure were completely uncorroded when trivalent chromium treated for 10 minutes or more and subjected to the permanganate post-treatment. There was only slight corrosion on panels treated 5 or 10 minutes and subjected to the peroxide post-treatment. Somewhat more corrosion was seen on the panels treated 20 or 40

1 minutes in trivalent chromium. In general, as found for the  
7075-T6 panels, the best corrosion resistance was obtained  
after 10 minutes treatment in trivalent chromium. With 2024-T3  
panels that were not subjected to a post-treatment, corrosion  
5 resistance showed considerable amounts of white salts.  
However, even the poorest of these were not nearly as badly  
corroded as bare (untreated) panels which were 95% covered with  
heavy white salts. The 2024-T3 panels showed self-healing  
properties at the scribe areas when a post-treatment was  
10 applied to those trivalent chromium treated 10 minutes or more.

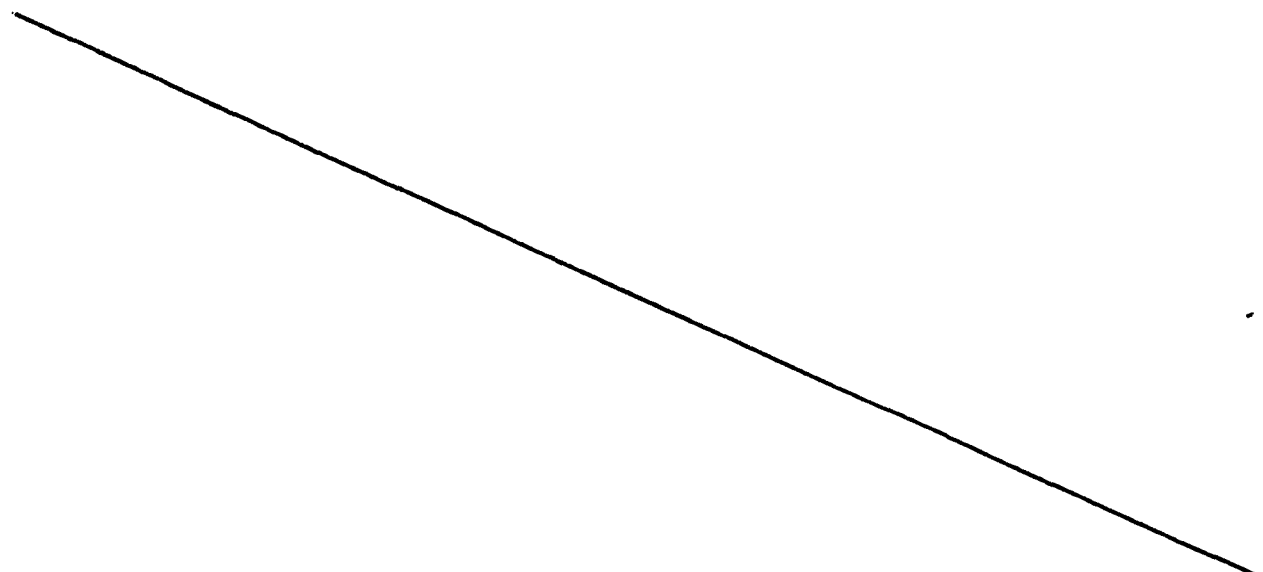
Self-healing is believed to be due to the hexavalent  
chromium introduced into the coating by the peroxide or  
permanganate post-treatment. A panel treated for 10 minutes in  
the trivalent chromium bath and post treated with peroxide was  
15 leached 30 minutes in 200 ml of boiling water. The water was  
found to contain 0.05 p.p.m. of hexavalent chromium. A control  
panel, not peroxide post treated, had no hexavalent chromium.  
Total chromium in the coating was determined by dissolving the  
films 5 minutes in 25% (vol.) HCl at 25°C and analyzing for Cr  
20 by atomic absorption spectroscopy. The solution contained 3.36  
p.p.m. Cr or 0.73 mg Cr removed per panel. This indicates that  
the films contain only about 19%  $[0.73/3.8 \times 100]$  of the films  
contain Cr. Hydrous chromic oxide would not account for more  
than about 40% of the film. It is, therefore, considered



1 likely that aluminum compounds comprise much of the film  
weight.

There was significant benefit in corrosion resistance to  
using permanganate post treatment over peroxide; however, the  
5 latter is simpler and less polluting and is preferred when  
optimum corrosion resistance is not required. The trivalent  
chromium bath treatment was even more effective for the  
protection of 6061-T4 aluminum than 7075-T6 or 2024-T3.

10 It is important to note that baths controlled by pH alone  
is not sufficient to ensure a good operating bath. However,  
the amount of alkali added is critical. Baths were prepared  
with 4 grams per liter of Fluka salt,  $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2 + 0.4 \text{ g/l}$   
 $\text{Na}_2\text{SiF}_6$  and various amounts of alkali added to obtain optimum  
pH. The baths were allowed to stand 2 weeks, pH measured,  
15 panels immersed 5 minutes at  $25^\circ\text{C}$  and subjected to a peroxide  
post-treatment. The results are as shown in Table II.



1

Table II

The data shows the effect of sodium hydroxide addition on the corrosion resistance of aluminum alloys treated in the trivalent chromium bath.

5

All panels were post treated in peroxide.

	Volume, ml N/2 NaOH Added/ Liter	pH After Standing 2 Weeks	Corrosion Rating* After Salt Spray Exposure					
			7075-T6			2024-T3		
			96 h	168h	336h	96h	168h	336h
	0	3.36	0	0	0	0	0	0
	4	3.51	0	0	0	0	0	0
	8	3.61	0	0	0	0	0	0
15	12	3.64	5	3+	3	4	3	2
	16	3.68	5	4	3+	4	3	2+
	20	3.71	5	4	4	4	3	2+

\*See Table I for Rating Key.

The data shows that there is a critical transition between 8 and 12 ml/l of 0.5N NaOH addition. Solutions with 8 ml/l or less NaOH addition were incapable of providing protection to aluminum while those with 12 ml/l or more provided effective protection. The difference in pH was minimal (3.61 vs. 3.64). It is important to note that there was no precipitation in the bath with 12 ml/l of 0.5N NaOH, slight precipitation with 16 ml/l and moderate precipitation with 20 ml/l. Results of salt spray exposure on the corrosion ratings are shown in the above table. There is some increase in corrosion resistance with increasing 0.5 N NaOH addition from 12 to 20 ml/l though the

1 bath with 12 ml/l added had the benefit of no loss of trivalent chromium through precipitation.

Additional panels were treated in the solutions containing 12, 16 or 20 ml/l of 0.5 N NaOH for only 2.5 minutes at 25°C.

5 The baths were then heated to 42°C and the tests repeated. The results of salt spray exposure tests on these panels are shown in Table III. All panels were post-treated in peroxide solution.

Table III

10 The data shows the effects of non-heated and heated trivalent chromium bath temperature on corrosion resistance of treated aluminum.

15

Volume, ml/l 0.5 N NaOH Added	Corrosion Rating* After 168 Hours Salt Spray Exposure			
	2.5 min. at 25°C		2.5 min. 42°C	
	7075-T6	2024-T3	7075-T6	2024-T3
12	0	0	3	2+
16	1	0	3+	3
20	2+	2	3+	3

20 \*See Table 1 for Rating Key.

Panels immersed 2.5 minutes at 25°C in the trivalent chromium baths were generally poor though the bath containing 20 ml/l 0.5 N NaOH provided substantially greater corrosion resistance than baths containing lesser amounts. Increasing

1 the bath temperature to 42°C considerably improved the  
corrosion resistance of panels immersed 2.5 minutes. Immersion  
of panels for 2.5 minutes at 42°C provided approximately the  
same corrosion resistance as panels immersed 5 minutes at 25°C.  
5 Thus, it has been demonstrated that increasing the trivalent  
chromium bath temperature can substantially reduce the required  
treatment time.

After the 12 liter bath was used to treat approximately  
150 panels (2.6 ft<sup>2</sup> per liter processed) the bath was reduced  
10 in effectiveness for providing corrosion resistance. However,  
it was found that addition of 0.4 g/l of Na<sub>2</sub>SiF<sub>6</sub> with a small  
amount of NaOH rejuvenated the bath to previous effectiveness.

Although basic chromium sulfate was used in the above  
tests, ordinary chromic sulfate (Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) is similarly  
15 effective. Trivalent chromium solutions other than sulfate  
have been studied briefly; chloride, nitrate or acetate was not  
as effective as sulfate. However, a simple solution of 2.5 g/l  
CrF<sub>3</sub>·9H<sub>2</sub>O properly adjusted with alkali showed some promise.

Preliminary tests showed that corrosion resistant films  
20 can be applied to aluminum by a wiping-on procedure using  
absorbent material soaked with the trivalent chromium solution.  
Post-treatment was applied, after rinsing, by a fine spray of  
dilute peroxide solution to cover the surface which was then  
allowed to dry. These results indicate that the process can be

1 used effectively for treating large surfaces for which an immersion process is impracticable.

Panels treated in the 12 liter trivalent chromium bath for 5 or 20 minutes, with or without peroxide post-treatment, were  
5 painted with epoxy primer (MILC-23377), aged one week, immersed in distilled water 24 hours at room temperature, dried, scribed and tape-tested in accordance with ASTM D3359. Bare panels failed the tape-test while all trivalent chromium treated panels, with or without post-treatment, passed the paint  
10 adhesion tests.

#### Sealing or treatment of Anodized Aluminum

Aluminum 2024-T3 alloy panels were anodized in 15% (weight) sulfuric acid solution for 30 minutes at 21°C at 18 volts. A trivalent chromium bath was prepared containing 5 g/l  
15  $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$  [Fluka Co.; 26%  $\text{Cr}_2\text{O}_3$  and 23 - 24%  $\text{Na}_2\text{SO}_4$ ] plus about 20 ml/l 0.5 N NaOH for use as a seal or treatment for anodized aluminum. The following seals were applied to the anodized aluminum:

a) Water Seal - 15 minutes in deionized water at boiling.

20 b) Dichromate Seal - 15 minutes in 5 g/l  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  at boiling.

c) Trivalent Chromium Seal

1                   A - Two minutes in above bath at boiling; rinse;  
                    two minutes in 10 ml/l  $\text{H}_2\text{O}_2$  (30%)

                    B - 15 minutes in above bath at boiling; rinse;  
                    two minutes in 10 ml/l  $\text{H}_2\text{O}_2$  (30%).

5                   The treated panels were exposed to salt spray for over  
3000 hours. The water sealed panels had considerable corrosion  
while the trivalent chromium seals were totally uncorroded.  
Thus, the effectiveness of a trivalent chromium seal or coating  
is well demonstrated. Immersion of anodized aluminum in the  
10                  trivalent chromium bath at room temperature provided corrosion  
resistance far superior to water sealed panels but not quite as  
resistant to those dichromate sealed. Moreover, deletion of  
the peroxide post-treatment did not seriously reduce the  
corrosion resistance of trivalent chromium sealed anodized  
15                  aluminum. It was also found that trivalent chromium seal  
coatings applied to chromic acid anodized panels were even more  
effective than dichromate with regard to improving corrosion  
resistance.

                    In formulating the coatings or seal compositions of this  
20                  invention, the chromium can be added conveniently to the water  
in any of its water soluble forms in which the valence of the  
chromium is plus 3. For example, the chromium may be  
incorporated in the form of  $\text{Cr}_2(\text{SO}_4)_3$ ,  $(\text{NH}_4)\text{Cr}(\text{SO}_4)_2$  or  
 $\text{KCr}(\text{SO}_4)_2$ . Mixtures of such compounds can be utilized. The

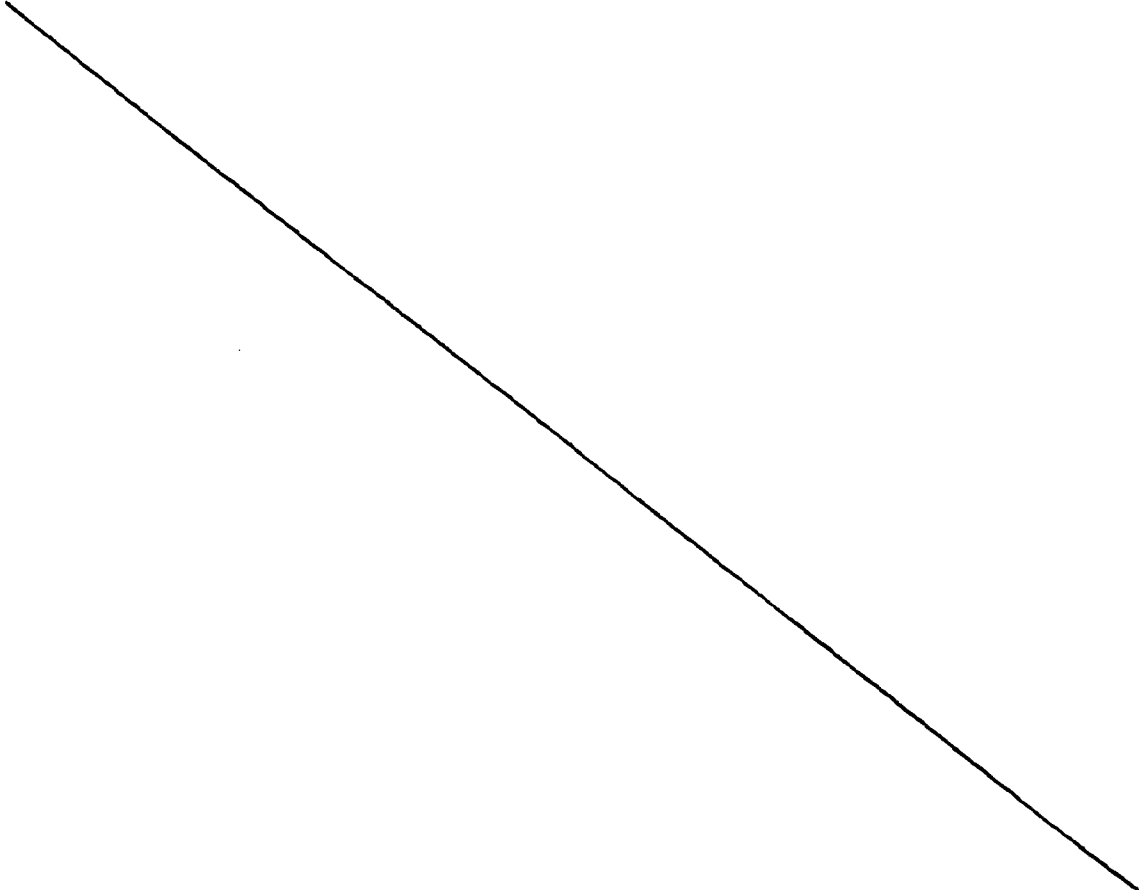
1 aluminum surface that is coated according to the present  
invention can be either pure aluminum or aluminum base alloys  
containing over 50% aluminum. The preferred trivalent chromium  
concentration is within the range of about 0.4 to 1.5 grams per  
5 liter by weight of the aqueous solution. It has been found  
that particularly good results are obtained economically when  
the chromium is present in this preferred range. With regard  
to the preferred fluoride addition to the bath, it is desirable  
that the amount of fluoride added range from about 0.1 to 0.6  
10 grams per liter. The complex fluoride such as fluorosilicate  
and not the simple fluorides are particularly preferred.  
However, fluoride addition is not required for anodized  
aluminum.

The treatment or coating of the aluminum surface can be  
15 carried out at various temperatures. For example, temperatures  
within the range of room temperature to about 90°F can be  
utilized. Room temperature treatment is preferred inasmuch as  
this eliminates the necessity for providing and operating  
heating equipment. The coating may be air dried or  
20 accomplished by any of the methods well-known in the art, for  
example, oven drying, forced air drying, exposure to infra-red  
lamps, etc.

Various paints or organic coatings can be used to paint  
the chromium treated aluminum as described in U.S. Patents  
25 2,231,407; 2,299,433; 2,479,409 and 2,675,334. Specific

1 coatings for the chromate treated aluminums particularly  
include the epoxy resins available from a variety of commercial  
sources. For example, "Epon 820" is an epoxy resin having an  
average molecular weight of about 380. Epon 828 has a  
5 molecular weight of 350-400 and an epoxide equivalent of about  
175-210. Epon 1001 is an epoxy resin having an average  
molecular weight of about 1000 and an epoxide equivalent weight  
of 500.

10 While various embodiments of the invention have been  
disclosed, the specific compositions and methods described  
herein are not intended to limit the scope of the invention.





1

5

10

15

20

25